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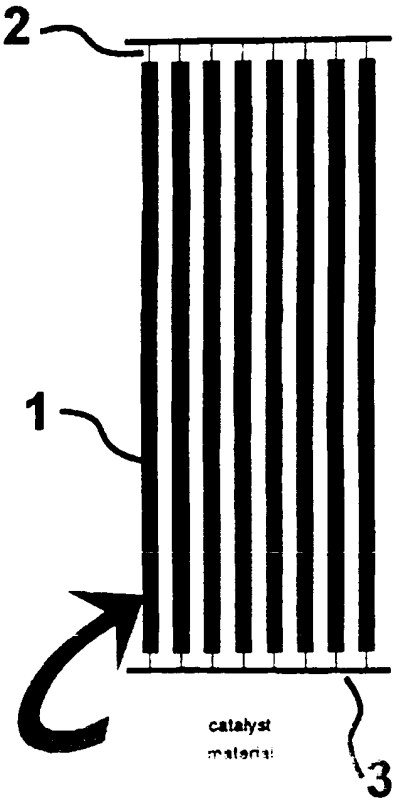
(54) Title: STRUCTURED REACTOR PACKING AND METHOD OF MANUFACTURING SAME

(57) Abstract

The invention comprises a method of manufacturing a catalyst element consisting of parallel rods of catalyst-containing material, which material has been provided around a rod-shaped support through pressing in a die. The invention further relates to structured catalyst packings consisting of elements manufactured according to this method. Finally, the invention relates to reactors provided with a structured catalyst packing manufactured with the method according to the invention.



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Title: Structured reactor packing and method of manufacturing same

The invention relates to a structured catalyst packing which is formed from a number of elements which comprise catalyst material, a method for manufacturing the elements, and a reactor provided with such a catalyst packing.

In a chemical reactor, to contact a solid substance, such as a catalyst, with a fluid, use is often made of fixed bed reactors in which catalyst particles have been poured more or less randomly. The fixed bed reactor owes its popularity to its simplicity, which manifests itself *inter alia* in relatively low investment costs. On the other hand, however, the fixed bed reactor often gives a considerable pressure drop, and the reactor clogs up fast if a gas flows through it which is contaminated with dust particles, such as fly ash. Another disadvantage is that the supply rate of heat through the wall of the reactor is very limited.

In reactors where gaseous reactants, optionally in the presence of liquid reactants, react over a fixed catalyst, the pressure drop across the reactor is of great importance with regard to the effectiveness and the efficiency, and hence the financial aspects of the conversion process in general. This problem is generally known and well recognized.

Thus, a pressure drop in excess of 10-20 mbar over a reactor for catalytically cleaning industrial flue gases leads to a financially unattractive process. In fact, the

consequences of the pressure drop have to be compensated by the employment of a fan to discharge the large volumes of cleaned flue gases via the stack.

Another example concerns the catalytic dehydrogenation of hydrocarbons and in particular alkanes. In this process, the pressure plays an important part. In fact, the degree of conversion of the feedstock in the reactor is limited by the thermodynamic equilibrium which is dependent *inter alia* on the hydrogen pressure. To overcome the pressure drop across the reactor, the pressure at the reactor inlet must be relatively high, which has an adverse effect on the reaction rate.

In order to reduce the problem of pressure drop, those skilled in the art have proceeded to provide a certain arrangement or structure in the catalyst packing.

An additional advantage of the use of structured catalyst packings is the lower sensitivity to any dust that may be present in the gas to be treated. This lower sensitivity is achieved by a geometric separation between fluid and catalyst. A reduced contact between these two phases leads to fewer collisions of dust particles in the gas with the catalyst and hence to less dust accumulation on or in the catalyst elements.

Moreover, a structured catalyst can be applied in gas/liquid/solids reactors that work according to the countercurrent principle. At high gas and liquid flow rates, loose catalyst packings - unlike structured catalyst

packings - give rise to maldistribution of the reactants and 'flooding' of the reactor with liquid.

On the ground of their morphology, the various reactors with structured catalyst packings can be subdivided into the following groups.

A first group includes reactors which are partly filled with gauze cages in which loose beds of catalyst particles are disposed. Depending on the type of reactor, the fluid flows alongside and/or through the cages. Known examples are the "parallel passage reactor" and the "lateral flow reactor".

The applicability of parallel passage reactors is limited by a low mass transfer rate in the catalyst beds. Owing to the circumstance that the gas is substantially stationary in the beds, except near the gauze walls, the mass transfer rate is limited to the effective diffusion rate in packed beds. Therefore the thickness of the beds may not be greater than about five times the diameter of the catalyst particles. At larger thicknesses, the inhibition of the reaction rate due to the mass transfer rate between the particles in the bed is stronger than the inhibition due to the pore diffusion rate in the particles. What is more, the costs of the gauze construction become disproportionally great in the case of beds thinner than 1 cm. These considerations impose a lower limit on the particle size, which is at approximately 2 mm. All this makes the application of the parallel passage reactor less attractive for processes with a high reaction rate.

The mass transfer problem of the parallel passage reactor is at least largely solved by providing for convective transport of reactants in the catalyst beds. The most effective method of realizing this is to alternately shut off the inlets and outlets of the channels through which the fluid flows, so that the fluid has to flow laterally through the beds. This results in a lateral flow reactor. A disadvantage of lateral flow reactors is that it is very complicated to provide for a good distribution of the flow through the reactor. Since the bed thickness is small, absolutely small variations therein may already lead to maldistribution of the fluid stream. Moreover, the dust resistance of this reactor is considerably lower than that of the parallel passage reactor and the reactors to be discussed hereinafter.

Other examples of reactors that are partly filled with cages in which loose beds of catalyst particles are disposed, are reactors that are used for so-called trickle-flow processes and for so-called catalytic distillation. In both known processes, both gas and liquid flow through a reactor in which a solid catalyst is present.

Trickle-flow processes are aimed at reacting a gaseous reactant with a liquid reactant, in the presence of a solid catalyst. Important advantages from the point of view of process technology are achieved by causing the gas and the liquid to flow countercurrently through the reactor.

Catalytic distillation is also aimed at reacting a gaseous reactant with a liquid reactant, in the presence of

a solid catalyst. In addition, however, in the same plant a physical separation is effected between the reactants and/or the products. This last requires the gas and the liquid to flow countercurrently through the apparatus.

In both trickle-flow and catalytic distillation, it is of importance to effect an intensive contact between the gas and the liquid, and between the liquid and the solid catalyst. An example of a trickle-flow reactor which has the above-mentioned characteristics is the so-called "Three-Level-Pore" (TLP) reactor. In this reactor, solid catalyst particles have been loosely poured into a relatively small trays of a diameter of a few centimeters, for instance of metal gauze, which are arranged in the reactor at certain intervals (in the direction of flow and perpendicularly thereto). Gas is forced from the bottom to the top through the reactor, whereby the gas will mainly flow between the trays with catalyst. At the top of the reactor, liquid is divided into drops and falls onto the uppermost trays with catalyst. Under the influence of gravity, the liquid flows down, mainly through the trays with catalyst particles owing to capillary forces. Owing to the gas and the liquid stream being geometrically separated from each other to a certain extent in this way, a low pressure drop is obtained. Moreover, it allows working at higher gas and liquid loads than in traditional reactors, filled completely with catalyst particles, without the occurrence of the problems, known to the skilled person, with regard to maldistribution

of gas and liquid, or flooding (the reactor fills up with liquid owing to the gas pushing the liquid back up).

An example of a reactor for catalytic distillation which has the above-mentioned characteristics has been described by Zheng and Zu in Trans I Chem E 70 part A (1992), 459-464. Catalyst material in the form of spheres of ion exchange resin (IER) with a diameter of from 0.3 to 1.2 mm is loosely filled into pockets of about 20 cm high and 2 cm wide. These pockets are formed by stitching hems of a width of 2 cm in two superposed layers of cloth of a height of 20 cm. The cloth of pockets filled with catalyst is then rolled up with a layer of corrugated gauze material, with the gauze providing for some distance between the pockets with the catalyst particles. The whole is then placed in a distillation column. The liquid then flows mainly through the pockets with the catalyst particles, whereas the gas flows mainly through the open spaces between the pockets. This provides the same advantages as mentioned in the last two sentences of the preceding paragraph.

Another example of a reactor for catalytic distillation which has the above-mentioned characteristics has been described by DeGarmo et al in Chem. Eng. Progr. (March, 1992), 43-50. In the so-called "Katamax" reactor packing, catalyst particles have been loosely poured between two parallel, corrugated sheets of metal gauze. The corrugations in the two parallel sheets can have the same direction but, for instance, may also be rotated 90° relative to each other. In both cases, the space between the two parallel

plates of metal gauze can easily be poured full with solid catalyst particles. The whole of the two plates of gauze with the catalyst particles between them, is designated by the term 'sandwich'. Several sandwiches are moved against each other in upright orientation, resulting in a packing. If the sandwiches are so constructed and stacked that the corrugations include an angle of, for instance, 45° with the main flow direction of the reactor in which the packing is placed, a so-called 'open crossflow' structure is obtained, which possesses the same pressure drop and lateral mixing properties for a gas stream as the known static mixers which are sold, for instance, by the Swiss company Sulzer.

A disadvantage the known reactors for trickle flow and catalytic distillation have in common is that the nature of the construction renders it unattractive to use thin or small cages, pockets or trays with catalyst particles. Then a relatively large amount of 'packaging material' (gauze, cloth) is required. Owing to the cages, pockets or trays being relatively thick or large, the catalyst is not always optimally utilized in the centre of the cages, pockets or trays. This is especially the case in relatively fast reactions, whereby the chemical reaction rate is greater than the physical diffusion rate of the reactants.

The second group of structured catalyst reactors is constituted by reactors in which very large catalyst elements are stacked, the reactor deriving its properties from the structure of those elements. A well known example of this type of reactor is the monolith reactor which

contains monoliths. Monoliths are ceramic bodies manufactured through extrusion, in which many parallel channels are located. The catalytically active material has been deposited in the porous channel walls. This type of reactors has a very low pressure drop. Moreover, the dust resistance of these reactors, both as regards the slowness of dust accumulation and the wear resistance in view of the abrasive action of dust particles, is relatively good.

It is noted that monolith reactors also have drawbacks. An important disadvantage is associated with the fact that the ceramic structure has a double function. On the one hand, the ceramic material constitutes the skeleton of the reactor, so that it must be strong; on the other hand, it constitutes the support for the catalytic material, which requires a large specific area. The necessary compromise has as a consequence that monolith reactors possess a relatively low specific surface, so that the activity per gram of catalyst is likewise relatively low.

More generally, existing catalysts are always a compromise between catalytic activity - which benefits from a highest possible porosity of the material - and mechanical strength - which, by contrast, benefits from a lowest possible porosity. This compromise exists in particular also for fixed bed reactors, into which the loose catalyst particles have been poured more or less randomly. The loosely poured particles must be strong enough to carry the weight of the particles on top of them and moreover to resist the force resulting from the pressure drop across the

bed. Any fracture of the catalyst particles can lead to clogging, which may or may not be local, of the catalyst. Further, the limitation of lateral transport to the diameter of the channels and the poor radial and axial heat transport in the monolith reactors are disadvantageous.

A last disadvantage of monolith reactors to be mentioned here is that the channels are smooth in the direction of the fluid flow, which, in combination with the dimension of the channels, leads to the flow being laminar under conventional process conditions. These smooth walls are due to the circumstance that the shape of the monolith is realized through extrusion. Although smooth walls are favourable with a view to reducing the pressure drop, they are not so with regard to the rate of mass and heat transfer.

A third group comprises reactors which are filled with structured packings on which catalyst material has been bonded or glued. An example of such a catalyst material comprises a ceramic or metal honeycomb structure on which a thin layer of material with a large surface has been bonded: the so-called washcoat. Usually, the catalytically active material is deposited on the washcoat. This type of reactors also includes reactors with structures of wires, gauze or thin plates to which catalyst particles have been applied using an adhesive.

An important advantage of this type of reactor over monolith reactors is that the functions of catalyst support and skeleton are separated. The skeleton can be optimized for strength and pressure drop; the washcoat can be

optimized for catalyst activity. The skeleton need not be manufactured through extrusion, so that the channels need not be isomorphous, which positively affects the mass and heat transfer values.

Washcoat reactors, by contrast, are less wear resistant than monolith reactors. Abrasion of the relatively soft washcoat will also lead to a rapid deactivation of the catalyst material applied thereto.

As stated, this third category of structured reactors includes wire, gauze or plate structures on which catalyst particles have been glued. The support material will as a rule be made of metal. This has as an advantage that it is possible to supply electrical heat to the catalyst. However, this possibility is limited in that the catalyst particles and the support material are as a rule separated from each other through a layer of glue which has a minor heat conductivity. An overt disadvantage is that the catalyst particles can only be used in a monolayer and the nature of the structure only enables the use of small catalyst particles which are substantially smaller than 1 mm. As a result, the fraction of catalyst volume in the reactor is limited. An inherent disadvantage of the use of a glue layer is that the particles are either partly recessed in the layer of glue, so that the active surface is limited, or have only a small contact surface with the support and thus are not strongly bonded.

European patent application 0378099 describes an apparatus for catalytic afterburning in a stack. This

apparatus consists of a system of two rings of different perimeter, from which rod-shaped ceramic catalyst elements are suspended. The ring that is largest in circumference is hung under the other. The catalyst elements are attached around the upper ring. The lower ring serves for hanging a part of the catalyst elements in an inclined position.

The catalyst elements used are ceramic moulded bodies. Not any method for manufacturing these elements is described.

This known structure, where catalyst bodies hang from a ring, moves under the influence of gas and/or liquid streams. This has as a consequence that the placement of such a structure in a reactor leads to pressure loss, which leads to higher energy costs. Moreover, the distribution of the flow through that reactor is less balanced, which leads to a non-optimal use of the catalyst. Nor does this known structure allow the catalyst bodies to be arranged so as to enable a lateral mixing of the gas and/or liquid stream.

European patent application 0416143 describes a catalyst system which consists of hanging rod-shaped catalyst elements. The rods hang from chains and can be hung higher or lower relative to each other. It is noted in this known European patent application that the rods can be formed from tin which is coated on two sides with catalyst material. In other words, tin with a washcoat is used. Just as in the system described in EP-A-0378099, the rods in this known system are not fixed, so that they move under the influence of a gas and/or liquid stream.

The placement and orientation of the rods as outlined in Fig. 1 of EP-A-0416143 has as a consequence that the resistance to gas and/or liquid flow is not the same everywhere, going from the centre of the structure to the outer edge. This leads to an unequal distribution of the gas and/or liquid flow across the structure, which in turn leads to a non-optimal utilization of the catalyst material. Moreover, this known structure is very difficult to scaled up. It is not properly possible to fill a reactor with a large diameter with the elements outlined in Fig. 1 of EP-A-0416143, in that they are round. When a reactor is hung full of such round structures, relatively large open spaces will be left between the elements, through which the gas and/or liquid stream will flow preferentially. This again leads to a non-optimal utilization of the catalyst. Accordingly, in view of the dimensions that are mentioned, only one such element is hung in the reactor (in this case a stack).

The object of the present invention is to provide a structured catalyst packing which upon application in a rector gives a heat and reactant transport rate between catalyst material and fluid which is comparable to that in a fixed bed reactor, combined with a low pressure drop, and a good mixing of fluid without costly separate mixing devices being required. In addition, the aim is for any different phases in the fluid, such as gas and liquid phases, to be properly contacted with each other. In effect, the object is to provide a catalyst packing which combines the advantages

of the known structured catalyst packing, while the disadvantages are not taken over.

In Dutch patent application 9000454, a so-called bead string reactor is described. This reactor is in fact an alternative to a parallel passage reactor with extremely thin catalyst cages having the thickness of a single particle. In particular, a bead string reactor is characterized by the fact that the catalyst material is attached to parallel wires ordered in a reactor. In practice, the reactor elements of a bead string reactor are manufactured by stringing commercially available hollow extrusions or annular pellets on a wire or rod; or by extruding a catalyst support material around a wire or rod. In particular when the catalyst material particles are relatively small or have a less well defined shape, the stringing process is relatively expensive.

The method whereby the support material is to be extruded around a wire, requires complicated equipment.

In fact, for extruding catalyst around a wire, the wire must be passed through, or possibly alongside, the extruding apparatus. Another disadvantage of the extrusion technique is the fact that the extruded structure is of the same shape in the direction of extrusion. No constrictions in the nature of Fig. 16 of Dutch patent application 9000454 can be obtained in the catalyst material. Utilizing the method according to Dutch patent application 9000454, only separate wires with catalyst material thereon can be obtained. These

separate wires must be fixed in a catalyst element in some manner or other.

Dutch patent application 9201940 describes a catalyst system wherein a structured support is covered with a layer of molecular sieve crystals, which sieve crystals are grown onto the support, so that they are chemically bound thereto. The method for manufacturing such catalyst elements, however, can only be used for a number of catalyst materials.

In the light of the two Dutch patent applications, the object of the present invention is to provide a method for manufacturing structured catalyst elements, which is simple as regards the method steps and is flexible as regards the choice of starting materials.

The present invention provides a catalyst element consisting of parallel rods of catalyst-containing material, which material has been provided around a rod-shaped support through pressing in a die, while the parallel rods are mutually connected, each rod being fixed at both ends.

An element according to the invention accordingly consists of parallel rods of catalyst-containing material which by means of pressing is physically contacted with a support material. This support material is rod-shaped, but can be provided with inwardly or outwardly directed irregularities or profiles in order to ensure a best possible physical bond between the support and the catalyst-containing element.

In effect, by pressing catalyst material onto or around a wire, basically any desired morphology of a catalyst material can be obtained. This provides advantages because, for instance, the change of the catalyst shape in the flow direction of the gas leads to improvement of mass and/or heat transfer. In addition, no loose wires with catalyst material are manufactured, which are subsequently fixed in some framework or other. By mutually connecting the ends on opposite sides of the rods, the structure is substantially immovable in a gas and/or liquid stream. According to the method of the invention, in a single pressing step a complete framework with catalyst supports is provided with catalyst material. Manufacturing complete frameworks-with-catalyst-supports is considerably simper than afterwards affixing loose supports on which catalyst material has been provided, in a reactor element.

The rods of catalyst-containing material are attached to an attachment means in that the rods comprise attachment means and not in that the rods are glued to the attachment means or are otherwise connected to the supporting rod through an adhesive. Although the rod-shaped support can basically be manufactured from any material that is compatible with the catalyst-containing material, it is preferably formed by a wire or rod of metal, glass (fiber) or plastic.

As stated, the support (including framework) is preferably in one piece. When, for instance, support means project into catalyst-containing pressed bodies on one side

only, this imposes strict requirements on the strength of the catalyst material. A major advantage of the method according to the invention, by contrast, is that the strength of the catalyst material as such need not meet very strict requirements. Due to the presence of the support means, the catalyst material is hardly subjected to mechanical load. Therefore the composition of the catalyst material can be optimized for catalytic activity. Any fracture of the catalyst-containing pressed body is then disadvantageous only when it breaks in the longitudinal direction, as a result of which it would come off the support means. When the pressed body breaks in other directions, the cracks formed will at most lead to a slightly increased pressure drop across the reactor packing.

When catalyst material which has been optimized for catalyst activity and is very porous and brittle, is not completely supported, it will soon yield under its own weight.

In particular, the rods obtained according to the method of the invention are held in position by mutually connecting the rod-shaped supports of the catalyst-containing rods by means of a framework of, for instance, metal or plastic. Possible connecting means are wires or rods of, for instance, metal, glass fiber or plastic.

Examples of elements according to the invention are shown in Figs. 1 and 2. As shown in these figures, the parallel rods of catalyst material 1 can include any desired

angle with the framework 3 to which they are attached by means of the rod-shaped support.

The invention further relates to a method for manufacturing catalyst elements, wherein rod-shaped support material and a powdered material are introduced into a die, the powdered material is pressed around the support material by closing the die and optionally treated further, so that a coherent whole is formed. Optionally, instead of a powdered material, a pasty material can be used as well. Such pastes contain substantially more water: powders typically contain less than about 6% water, pastes mostly 20-40%.

Further, instead of a powdered material, granular catalyst material, for instance ion exchange resin (IER) in the form of spheres with a diameter of between 0.3 and 1.2 mm can be used.

The elements are manufactured by pressing powder, paste or granules around the mutually fixed attachment means, using a die. All this is diagrammatically shown in Fig. 3.

In a preferred embodiment, a die 4 is partly filled with powder. This powder can for instance, and preferably so, consist of (a mixture of) substances which upon further treatment, such as drying and baking, can serve as catalyst support material, such as silica, alumina or clay, optionally mixed with substances which promote the coherence of the powder upon pressing: the binders known to those skilled in the art.

In the practice of the present invention, suitable powders are used which are also used in the manufacture of the catalyst pellets known to those skilled in the art.

The manufacture of catalyst pellets, which consist of loose particles, through compression of powder, is concisely described in the following two publications:

- Satterfield, C.N., 1991, "Heterogeneous Catalysis in Industrial Practice", McGraw Hill, Inc., New York, Chapter 4, specifically section 4.2.2; and

- Stiles, A.B., 1983, "Catalyst Manufacture-Laboratory and Commercial Preparations", Marcel Dekker, Inc., New York. Chapters 8 and 9.

The materials and techniques that are used for pressing catalyst pellets are also suitable for manufacturing the structured elements disclosed in the present specification.

Suitable powdered materials for use as support material for the catalyst are alumina, silica, and various clays, in particular types of clay consisting of mixtures and compounds of silica, alumina and magnesia. When using these materials, after pressing, catalytically active material must be deposited on the support material by means of impregnation. This technique is known to those skilled in the art. Catalysts manufactured in this way are sometimes referred to as 'impregnated catalysts'. In addition, it is possible to use powder which contains components which, optionally upon further treatment, exhibit catalytic activity. In this case, the powder can contain, for instance, copper oxide, zinc oxide, magnesium oxide, copper

chromite, nickel chromite and/or molybdates, optionally in combination with alumina and/or silica. Catalysts manufactured in this way are sometimes referred to as 'precipitated catalysts', because the powder, for instance copper oxide, has mostly been obtained through precipitation of salts from a solution. Further, the powder can contain zeolites. Zeolites, also referred to as 'molecular sieves', or 'mol sieves' for short, constitute an important class of catalytically active materials which are currently witnessing a marked increase in popularity. These zeolites can be used in combination with alumina and/or silica.

To be able to manufacture a coherent product through the pressing of such powders, the powder should preferably be slightly moist. Thus, good results are obtained when 3-6% water or nitric acid is present. Further, it is preferred to add small amounts of two types of additives. In the first place, lubricants are mentioned, such as graphite (0.5-3%), stearic acid, polyvinyl alcohol, polyethylene or other types of waxes and fats (all 2-4%). The percentages mentioned are percentages by weight, and are typical though not limitative figures. These substances limit the wear of the pressing equipment and of the resultant catalyst particles as they are removed from the die. In addition, binders are used, such as clay, colloidal or hydrated alumina or colloidal silica. The amount of binder can vary from a few per cent to tens of per cents.

In the partly filled die 4, of which a top plan view is shown in Fig. 3c, a framework 3 with connecting means 2 as

shown in Fig. 3d can then be placed. Then the die can be filled up with a sufficient amount of the powder. Then the die is closed by means of an upper die or punch 5; all this as shown in Figs. 3a and 3b. During this treatment the powdered or pasty material is strongly pressed together and onto the support, so as to yield a coherent whole.

Conventional pressures for the purpose of pressing pressed bodies according to the invention are of the order of magnitude of 20-200 bar. The higher the pressure, the greater the mechanical strength of the catalyst particles, but also - in general, at least - the lower the porosity and, as a consequence, the catalytic activity. Lower pressures are also possible, because the catalyst material need only have a very minor mechanical strength. In this way, catalyst material with a higher porosity and hence a higher activity/effectiveness can be manufactured.

The coherent whole of framework 3, connecting means 2 and the pressed powder mass can thereafter be optionally treated further. Thus the whole can be baked or dried in the die, or be removed from the die and thereafter be treated further.

If the powdered or pasty mass did not yet contain any catalytically active material, or if more or other catalyst material is to be added to the pressed mass, the rods of catalyst support material can be provided with catalytically active material. For providing catalytically active materials on and/or in the catalyst support material, many methods are known. A widely used method consists in

impregnating the support material with a solution that contains salts of catalytically active material, whereafter through annealing in a suitable atmosphere the material is brought into the desired chemical form. For that matter, it is also possible to mix the salts of catalytically active material with the powder or the paste prior to pressing and to carry out the annealing operation afterwards.

If the powdered or pasty mass with which the rods have been manufactured, contain zeolites or clays, this material can also be rendered catalytically active by introducing different types of ions, for instance metal ions, via the technique of ion exchange, known to those skilled in the art.

In a different embodiment than that where powdered or pasty material, for instance based on silica, alumina, zeolites or clays, is used as starting material for the manufacture of the catalyst rods, granules of ion exchange resin (IER) are used as basic material. IERs consist of polymers, such as polystyrene, which exhibit more or less a network structure (cross-linking) and which possess so-called functional groups. These functional groups comprise, for instance, sulfonic acid groups or amine groups, and enable the IER material to include or exchange ions. IERs are used *inter alia* for softening water and for catalyzing reactions in which an immobilized, strongly acid catalyst is necessary, such as in the synthesis of the industrially important product methyl-tert-butylether (MTBE). With reference to the embodiment with powdered and pasty basic

material, it has been mentioned that additives such as water or nitric acid are necessary, as are certain binders. In the embodiment with IER the additives consist of water and/or organic solvents such as toluene or styrene, which is adsorbed into the granules. During pressing, at a pressure between 2 and 20 bar and at an elevated temperature of, for instance, 50-200°C, the granules start to stick together through partial fusion, through physical bonds and/or chemical reaction. A possible post-treatment method for the rods made up of IER spheres consists in introducing ions through ion exchange.

The present invention moreover provides structured packings made up of elements consisting of parallel rods of catalyst material, which are attached to attachment means. Thus a catalyst packing is formed which consists of at least two catalyst elements according to the invention, which elements are ordered relative to each other in a direction perpendicular to the parallel rods.

Examples of such structured packing units of catalyst material according to the present invention are shown in Figs. 5-7, with the individual elements being represented schematically in side and top plan view in Fig. 4. All this makes it possible to place and orient the catalyst rods in such a manner that the flow resistance for the gas and/or liquid stream is equally large at all points. Therefore the flow can be distributed in a highly balanced manner and the catalyst material is optimally utilized.

In a preferred embodiment, in the packing according to the invention the individual catalyst elements are arranged relative to each other in such a manner that fluid particles cannot move in a straight line through the packing. An example of such an embodiment is shown in Fig. 6 when the front of the fluid stream runs parallel to the catalyst elements. Thus the fluid particles are brought into contact with the catalyst-containing rods with a greater probability.

The relative distance between the parallel rods in the elements according to the invention is 0.1-3 times the diameter of the rods. A smaller relative distance leads to a pressure drop across the structured catalyst packing that is unacceptably high for most practical applications. A greater distance leads to a packing which is filled with catalyst material for a (mostly unacceptably) small fraction.

In the case of a packing according to any one of Figs. 5-7, where the parallel rods of catalyst material within an element are disposed parallel to the framework, the relative distance between the elements is preferably 0.1-3 times the diameter of the rods, for the same reason as mentioned in the preceding paragraph.

If within an element the connecting means 2 are not attached perpendicularly to the framework 3, it is advantageous to arrange the elements alternately in mirror-image configuration, as shown in Figs. 8 (a)-(c). What is accomplished by such an alternate arrangement is that a fluid element cannot move through the packing in a straight

line. Each fluid element is forced by the packing to move through the packing along a zigzag pattern. This leads to a mixing of fluid in the lateral direction, that is, transverse to the main stream direction. This mixing is many times more effective than the lateral mixing in existing reactors with structured catalyst packings, and even so effective as to render the use of costly mixing equipment superfluous.

The structured packing units according to Fig. 8 especially effect lateral mixing in the direction parallel to the elements. With advantage, two or more of such structured packing units are arranged in series, with successive packing units being rotated 90° relative to each other in the lateral plane. Thus, viewed across two successive packing units, a particularly effective mixing of the fluid in both lateral directions is effected.

In the case of a packing according to Fig. 8, where within an element the parallel rods of catalyst material are not attached perpendicularly to the framework and the elements have been ordered alternately in mirror-image configuration, the elements are preferably arranged against each other. This leads to the most effective lateral mixing.

The catalyst packings according to the invention make it possible to provide a reactor with a low pressure drop, which reactor can even be utilized in applications where the reaction conditions comprise a low pressure or high space velocities. The accumulation of dust is low, while the catalytic support material, either by the moulding pressure

used or as regards the material choice, is protected sufficiently against an abrasive action of dust particles present in the fluid.

The catalyst packings according to the invention also make it possible to provide a reactor which is particularly suitable for processes in which gaseous reactants react with liquid reactants in the presence of a solid catalyst, while both phases can flow cocurrently as well as countercurrently. Examples of such processes are trickle flow processes (for instance for hydro-desulfurization of gas oil) and catalytic distillation (for instance in the synthesis of MTBE). In such so-called three-phase processes, the structure of the catalyst packing leads to the low pressure drop mentioned earlier, and moreover to a favorable, proportional liquid and gas distribution over the packing. As a result, the processes can be operated with a high selectivity and a good contact between the three phases at high gas and liquid loads without involving maldistribution or flooding. An important advantage of the present invention over the prior art resides in the fact that relatively thin catalyst rods can be used, which are in direct contact with the gas and/or liquid stream. Thus the catalyst material is used optimally.

Through a suitable relative arrangement of the elements according to the invention, a turbulent fluid flow in the reactor can already be obtained at relatively low Reynolds numbers. As a result, the mass and heat transfer between the different fluid phases, if any, (for instance gas and liquid

phase) as well as between the fluid and the catalyst phase is high.

When the support of the catalyst-containing rod is made of a good heat conducting material, for instance of metal, it is possible to use this support as an electrical heating element, so that for a number of applications relatively thick rods of catalyst-containing material can be used.

CLAIMS

1. A catalyst element consisting of parallel rods of catalyst-containing material, which material has been provided around a rod-shaped support through pressing in a die, and wherein the parallel rods are mutually connected, with each rod being fixed at both ends.

2. An element according to claim 1, wherein the rod-shaped support is a wire or rod of metal, glass or plastic.

3. An element according to claim 1 or 2, wherein the relative distance between the parallel rods is 0.1-3 times the diameter of the rods.

4. A catalyst packing consisting of at least two catalyst elements according to one or more of the preceding claims, which elements have been arranged relative to each other in the direction perpendicular to the parallel rods.

5. A packing according to claim 4, wherein the separate catalyst elements are arranged relative to each other in such a manner that fluid particles cannot move through the packing in a straight line.

6. A method for manufacturing catalyst elements, wherein rod-shaped support material and a powdered, paste-like or granular material are introduced into a die, the powder, paste-like or granular material is pressed around the support material through closure of the die and is optionally treated further so that a coherent whole is formed.

7. A method according to claim 6, wherein the powdered, pasty or granular material is formed by silica and/or alumina and/or clay and/or ion exchange resin, optionally in combination with a binder.

8. A method according to claim 6 or 7, wherein the powdered, pasty or granular material comprises catalytically active material.

9 A method according to any one of claims 6-8, wherein supplementary catalyst material is provided on and/or in the coherent whole.

10. A reactor comprising a packing according to claim 4 or 5.

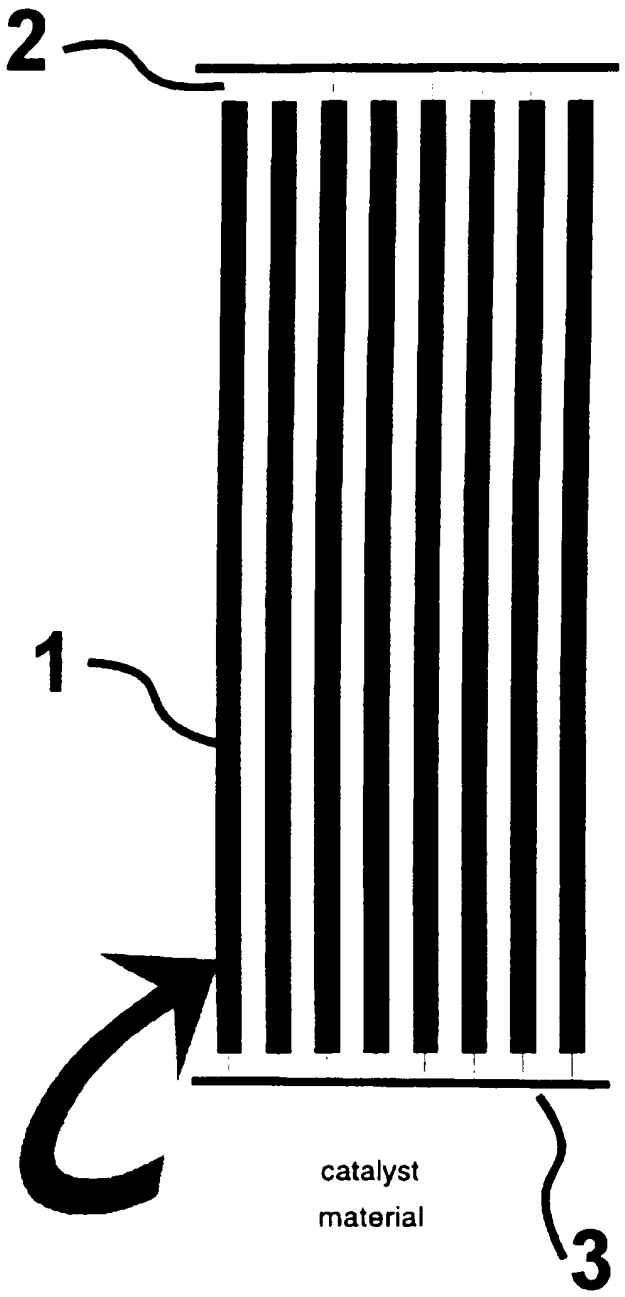


Fig. 1

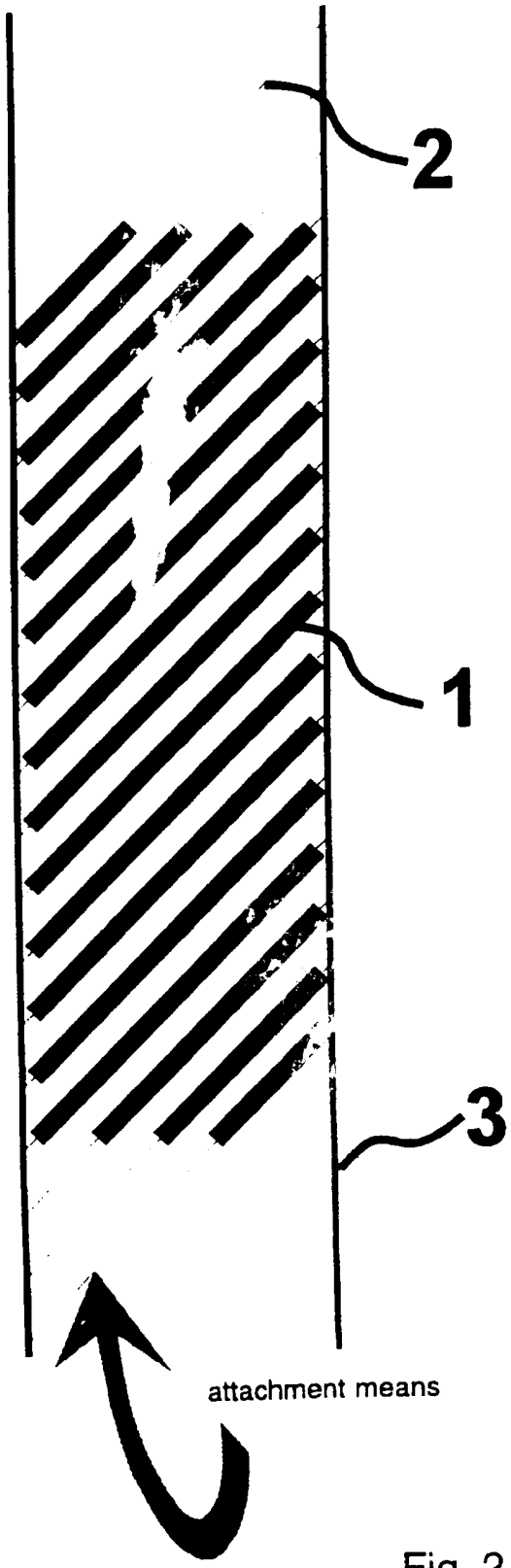


Fig. 2

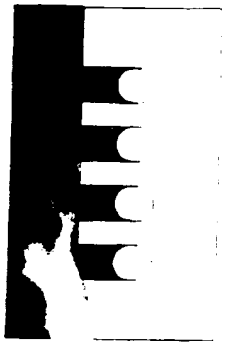


Fig. 3b

side elevation of mould

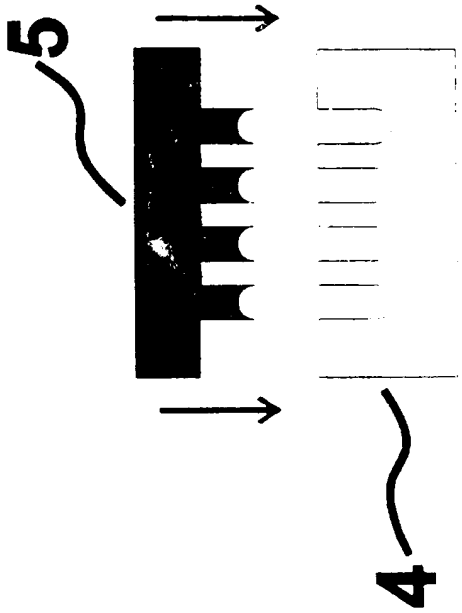
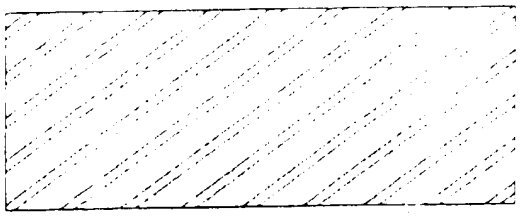
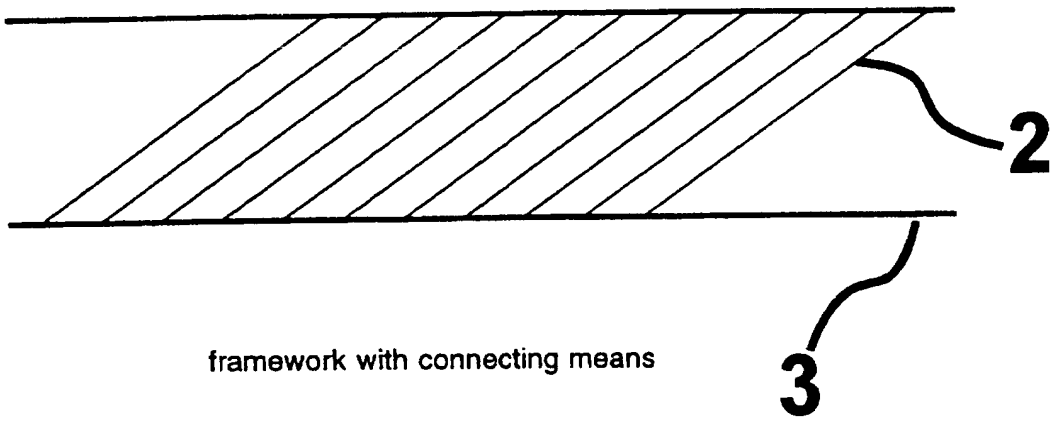


Fig. 3a



top plan view of mould

Fig. 3c



framework with connecting means

Fig. 3d

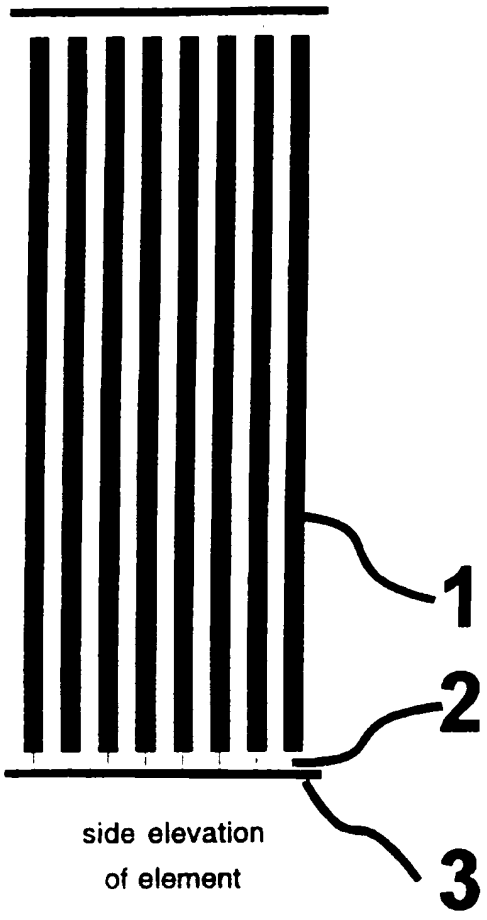


Fig. 4a

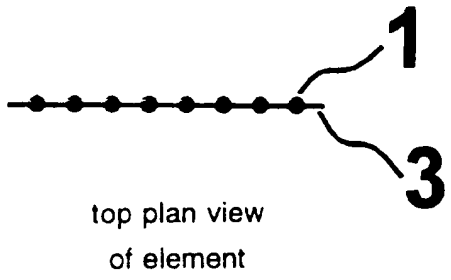


Fig. 4b

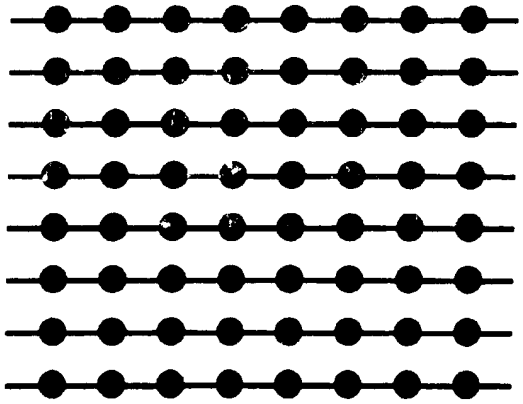


Fig. 5

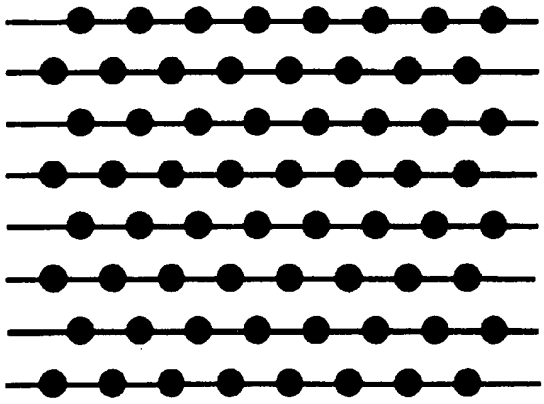
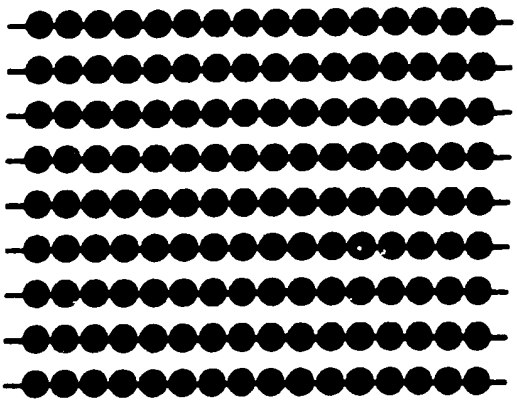


Fig. 6

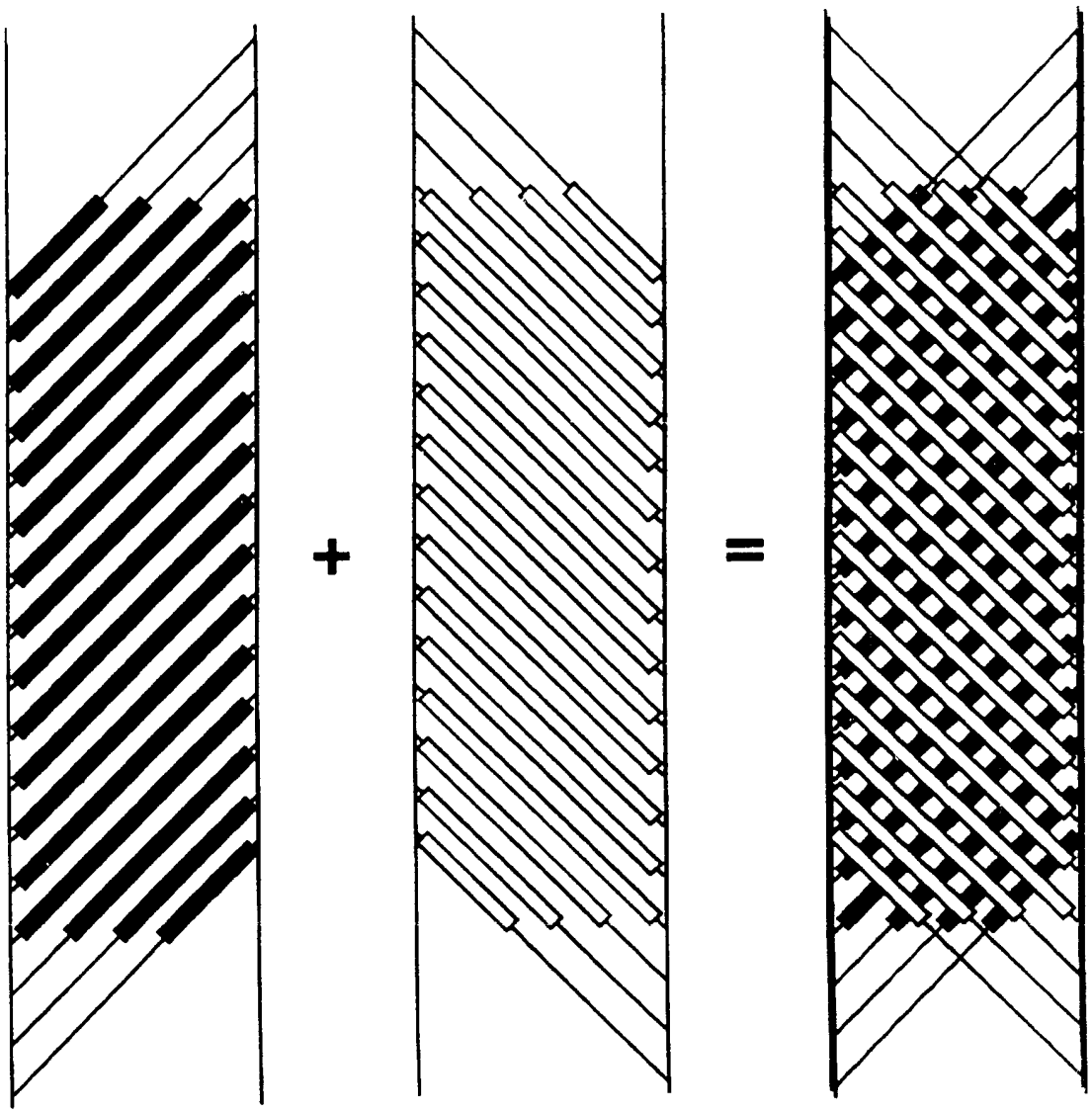


top plan views of a few possible structured packing units

Fig. 7

top plan view of elements

Fig. 8A



side elevations of elements

Fig. 8B

top plan view of structured packing unit

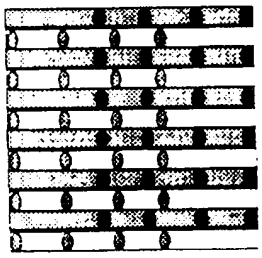


Fig. 8C

INTERNATIONAL SEARCH REPORT

National Application No
PCT/NL 96/00168

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J35/02 B01J35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 378 099 (HORST GUNTER) 18 July 1990 see claim 1 see figures 1-3 see column 2, line 51 - column 4, line 10	1
A	EP,A,0 416 143 (GRS GES REAKTORSICHERHEIT) 13 March 1991 see figures 1,2,7 see column 3, line 37 - line 52	1
A	EP,A,0 226 306 (ICI PLC) 24 June 1987	
A	DE,U,84 37 188 (KLEIN) 2 May 1985	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
18 July 1996	29 -07- 1996

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Thion, M

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No
PCT/NL 96/00168

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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EP-A-0416143	13-03-91	DE-D-	58908947	09-03-95
		RU-C-	2012392	15-05-94
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		CA-A-	1273623	04-09-90
		JP-C-	1761812	28-05-93
		JP-B-	4045215	24-07-92
		JP-A-	62114658	26-05-87
		US-A-	4743578	10-05-88
DE-U-8437188	02-05-85	WO-A-	8603822	03-07-86
		EP-A-	0203976	10-12-86